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New Organic Ligands in Complexes of Transition Metals

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Results obtained for complexes of transition metals with unusual organic ligands—trimethylenemethane, tetramethylene-ethane, pentadienyl, and benzyl—are summarised. The chief structural and chemical features of these compounds are discussed. A list of 169 references is included.

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I. INTRODUCTION

The development of the chemistry of organic derivatives of transition metals, the vigour of which strikes the imagination, has not weakened even after twenty years have elapsed. Since the discovery of ferrocene it has become evident that any organic molecule can be in some way bound to a transition metal. Alkyl, aryl, and mixed radicals, as well as an acetylene residue, are able to combine with the metal by a simple σ-bond. Mono-, di-, and poly-enes—acyclic and cyclic, conjugated, unconjugated, and cumulated—aromatic and non-aromatic hydrocarbons and heteroatomic compounds form the most diverse π-complexes, frequently of unexpected structure. Besides such types of complex formation, which have already become usual, fresh possibilities have been revealed during recent years in this apparently exhausted field. It was demonstrated theoretically and confirmed experimentally that unstable organic species are stabilised significantly by complex formation. This provided a means of fixing and investigating such molecules as cyclobutadiene, such biradicals as trimethylenemethane and tetramethylene-ethane, and ions of the benzenonium type, which are extraordinarily difficult or quite impossible to study in the free state.

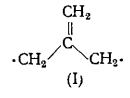
Complexes of various carbenes have been obtained. Furthermore, new possibilities have been revealed for the coordination of stable molecules. For example, an aromatic molecule is able to combine with a metal by an individual link, besides the "normal" type of bonding (as in π-arene complexes). This raises the problem of the stability of aromatic systems in the presence of transition metals.

The present Review discusses complexes with relatively new organic ligands—trimethylenemethane, tetramethylene-ethane, π-benzyl, and pentadienyl—surveying the conditions of formation as well as their physical and chemical features. Together with the π-benzyl complexes an attempt has been made to examine also the available factual information on the fragmentary coordination of aromatic molecules with metals. Work published up to December 1971 is covered.

II. π-COMPLEXES WITH TRIMETHYLENEMETHANE AND TETRAMETHYLENE-ETHANE

1. Trimethylenemethane—Structural Characteristics of the Free Biradical and of the Trimethylenemethane Ligand

The unstable reactive species trimethylenemethane (I) should theoretically have a triplet ground state (i.e. be a biradical) with a strongly delocalised system of four π-electrons[1] (delocalisation energy 1.46 β). Trimethylenemethane is important for theoretical chemistry because its central carbon atom forms a bond of maximum order ($N = 1.732$) and has the minimum free valency ($F = 0$). These are the extreme values possible for unsaturated carbon[2].

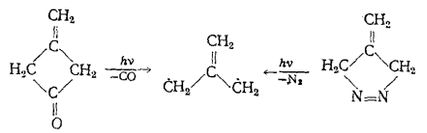


(I)

The molecule (I) has been examined as a model in various theoretical calculations[3-7] and has been assumed as an intermediate species in the thermal decomposition of 4-methylene-Δ^1-pyrazoline[8] and esters of 2-methylene-propane-1,3-diols[9], the thermal isomerisation of methylenecyclopropanes[10], the action of alkali metals on 3-halogeno-2-halogenomethylpropenes[11,12], and other reactions[13,14]. The chemical processes involving trimethylenemethane and its closest homologues and heteroanalogues have been reviewed[15].

The calculated carbon — carbon bond lengths of ~1.42 Å [6,16] and the first ionisation potential of 8.62 eV [16] have been confirmed experimentally in investigations of complexes of trimethylenemethane with the tricarbonyl-iron group[16-20]. The singlet form of trimethylenemethane is probably generated in thermal processes[16-22]. The triplet character of trimethylmethane and the equivalence of all six hydrogen atoms have been confirmed experimentally. By means of the electron spin resonance spectra Dowd observed this species among the products of

the low-temperature photolysis of 4-methylene-Δ^1-pyrazoline and 3-methylenecyclobutanone (at about −200°C):[23-25]



At this temperature the spectrum of trimethylenemethane remains for a month, but even at −150°C it changes instantly and irreversibly.

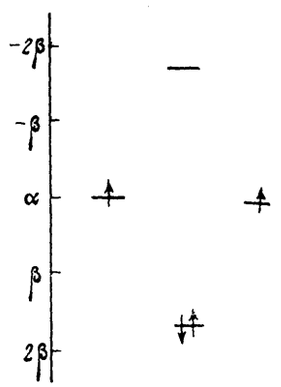


Figure 1. Energy-level diagram of the π-system of trimethylenemethane obtained by the Hückel molecular-orbital method.

Fig. 1 shows the energy levels of the π-system of trimethylenemethane.

As in other cases, this biradical is stabilised by forming a complex with a transition metal. It can reasonably be assumed that bonding occurs by interaction of the lowest filled molecular orbital with the sd_{z^2} hybrid orbital of the metal and of the doubly degenerate molecular orbital of symmetry E with the d_{xy} and d_{yz} orbitals of the metal. Probably no significant use is made of the highest molecular orbital $A_2(2)$, which is strongly antibonding, although no calculations have been made of the overlap integrals.

Existing experimental information shows that trimethylenemethane combines especially readily with the tricarbonyliron group, and its complexes are comparable with those of cyclobutadiene with respect to choice of metal and other partners. On the other hand, as will be shown below, direct transitions are possible from allylic complexes to trimethylenemethane, and *vice versa*. Thus the chemistry of compounds of this new ligand is also closely similar to that of π-allylic derivatives.

X-Ray[17,18,26,27] and electron[19,20] diffraction investigations of trimethylenemethane complexes indicate the equivalence of the bonds in the ligand, which is uniformly bound to the iron atom located exactly above the central carbon atom (Fig. 2). The $Fe-C_{(4)}$ distance is 1.93 Å both in the crystal and in the gaseous state; it is rather smaller than the distance (2.06 Å) from iron to the plane of the ligand in tricarbonyl(cyclobutadiene)iron. However, the distance from iron to the terminal carbon atoms (2.09 − 2.16 Å) is rather longer. The C − C bond lengths in coordinated trimethylenemethane are ~1.40 Å. Both methods show that $C_4H_6Fe(CO)_3$ has C_{3v} molecular symmetry with a crossed relative arrangement of the ligands (a trigonal antiprism). The central carbon atom of the trimethylenemethane system emerges to between 0.31 [18] and 0.22 [26] Å from the plane of the other three carbon atoms, on the side opposite to the metal. The phenyl-substituted complex exhibits[18] non-coplanarity of the substituent and the adjacent carbon atom (angle of deflection 59°), which should diminish the degree of $p_\pi - p_\pi$ interaction between the fragments. Possibly for this reason the introduction of a phenyl substituent into the trimethylenemethane system does not affect the positions of the absorption bands due to carbonyl groups[28].

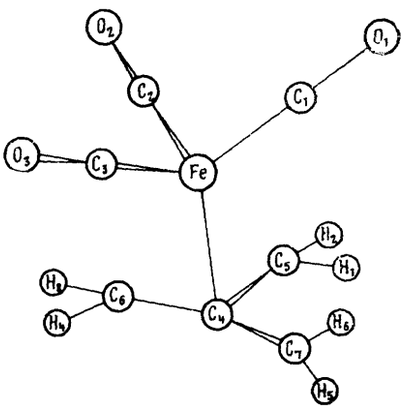


Figure 2. Structure of tricarbonyl(trimethylenemethane)-iron[20].

The nuclear magnetic resonance spectra of ^1H- and ^{13}C-tricarbonyl(trimethylenemethane)iron show that all six protons are magnetically equivalent and have a chemical shift of ~2 ppm,[29] which is in the region of absorption by the terminal protons of π-allylic and π-butadiene derivatives of iron. The spin − spin interaction constant $I_{^{13}C,H} = 162$ c/s, which is also typical of ethylenic π-complexes.

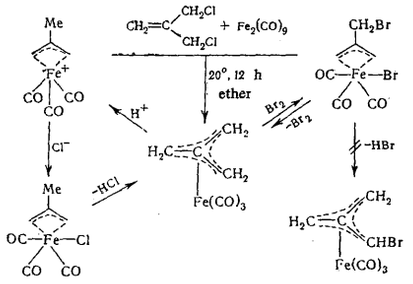
The complexes reported at the present time have in the infrared spectrum two or three carbonyl-stretching absorption bands according to the local symmetry of the carbonylmetal group $M(CO)_n$.[28-30]

2. Condition of Formation and Chemical Reactions of Trimethylenemethane Complexes

The trimethylenemethane complex was first obtained by Emerson and his coworkers[29] by the reaction of 3-chloro-2-chloromethylpropene with iron nonacarbonyl (Scheme 1). They also found that the new complex easily adds hydrogen chloride with conversion into a known allyl derivative of iron. Subsequently these workers developed this observation and found the conditions for the reverse transformation from substituted allyl complexes to trimethylenemethane derivatives[31]. This reaction occurs simply on

fractional distillation of the mixture formed by interaction between an allyl halide and iron nonacarbonyl. The first stage yields an allyl complex, which need not be isolated. The yields of trimethylenemethane derivatives obtained by this method reach 30%. Propenes and sometimes diene complexes of iron are obtained as side-products.

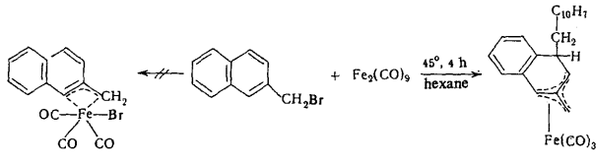
Scheme 1



Scheme 1 shows that tricarbonyl(trimethylenemethane)-iron is able also to add bromine reversibly. The resulting tricarbonyl(2-bromomethylallyl)iron bromide could be degraded in two ways—elimination of hydrogen bromide with formation of a complex containing a brominated trimethylenemethane ligand or elimination of bromine to return to the original complex—the latter of which actually occurs.

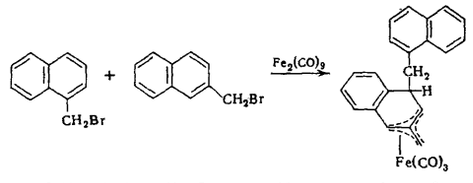
The salt $NaFe(CO)_4$ can be used instead of iron nonacarbonyl in the above reaction[30], which somewhat increases the yield of the complex.

Unusual conditions for obtaining the trimethylenemethane system have been found by Nesmeyanov and his coworkers[26,27,32,33]. This system is formed from 2-bromomethylnaphthalene, which under the conditions indicated adds the naphthylmethylene radical to one of the double bonds of the substituted ring:



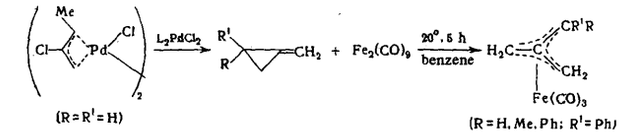
The extremely mild conditions of this transformation and the accompanying breakdown of the aromatic structure of the naphthalene molecule indicate that the nature of the trimethylenemethane ligand conforms well to the electronic and steric requirements of iron and that it is preferred to allyl.

The naphth-1-ylmethyl radical is able to take part in this reaction only as an adduct:



Formation of the trimethylenemethane system from 1-methylnaphthalene would have entailed breakdown of the aromatic structure of the second ring as well, and obviously this cannot be compensated even by formation of a bond with a metal. Several extremely stable compounds have been obtained under the above conditions, including the first complex of trimethylenemethane containing halogen in the ligand (Table 1). X-Ray diffraction examination of one of these compounds[26,27] enabled the structure of the complexes obtained to be understood correctly, and showed that the chief molecular parameters are general both for higher analogues and for the simplest complexes of trimethylenemethane.

Ring-substituted methylenecyclopropanes undergo ring-opening in the presence of iron carbonyl, and then coordinate with the iron as the trimethylenemethane form[28]:



The yields of the complexes reach 40 — 60%, but in the absence of substituents in the three-membered ring only tricarbonyl(butadiene)iron is obtained.

Table 1. Summary of data on complexes with trimethylenemethane and tetramethylene-ethane*.

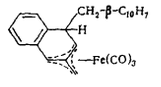
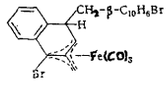
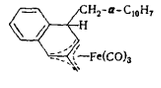
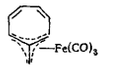
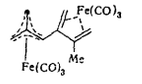
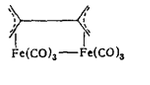
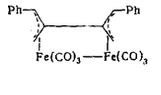
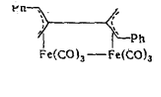
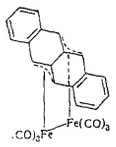
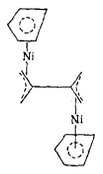
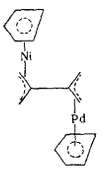
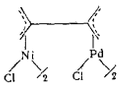
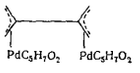
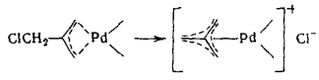
Metal	Compound	Colour	M.p., °C	Ref.
Cr	$(CH_2)_3CCr(CO)_4$	yellow	83	30
Mo	$(CH_2)_3CMo(CO)_4$	yellow	50	30
Fe	$(CH_2)_3CFe(CO)_3$	light yellow	33	19, 28–31
	$PhCH(CH_2)_2CFe(CO)_3$	—	64	18, 28, 31
	$MePhC(CH_2)_2CFe(CO)_3$	—	liquid	28
	$Ph_2C(CH_2)_2CFe(CO)_3$	—	158	28
		light yellow	142	33
		light yellow	175	33
		light yellow	100	26, 27, 33
		—	41	57
		lemon yellow	118	47
		red	89	43, 45
		dark red	131	48
		orange-red	190	48

Table 1 (contd.)

Metal	Compound	Colour	M.p., °C	Ref.
		orange	214	56
Ni		dark red	cryst.	54
Ni, Pd		red	160 (decomp.)	54
		brown	cryst.	54
Pd		white	cryst.	55

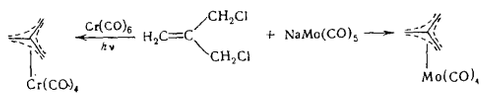
*In this and subsequent tables a dash in a column means that the characteristic is not given in the original paper.

A quite different result—formation of complexes with a π-allylic ligand—ensues when methylenecyclopropane undergoes ring-opening under the influence of palladium salts[34]. On the other hand, n.m.r. data confirm the formation of a fairly stable intermediate species, probably of the trimethylenemethane type, in the solvolysis of 2-chloromethylallyl complexes of palladium[35]:



Thus methylenecyclopropane obviously behaves differently in the presence of iron and of palladium, perhaps because of different states of the trimethylenemethane formed when the ring is opened.

A few complexes of trimethylenemethane with Group VI metals have been prepared[30]:



The conditions of their formation are clear from the above scheme. However, the yields are very low.

The list of compounds containing a trimethylenemethane ligand is not yet very long (Table 1). It is evident that they are all quite stable substances, melting at fairly high temperatures (often with decomposition). The thermal stability of the complexes is greatly improved by the introduction of phenyl substituents. The naphthalene derivatives melt without decomposition at 140 – 170°C, and are the most stable. The stability of the trimethylenemethane complexes also governs their behaviour in the mass spectrometer. All the compounds studied give molecular ions[29,33]. These compounds are considerably less stable in solution than in the solid state.

As with most other types of π-complexes, structural investigations predominate over chemical studies in this case. This is obviously due to the relative inaccessibility of these compounds and their comparative instability in solution. Besides the above addition of bromine and hydrogen chloride, the oxidation of tricarbonyl(trimethylenemethane)iron by a quadrivalent cerium salt has been studied[30], which obviously results in the liberation of trimethylenemethane. In any case, an adduct of the latter compound is obtained in the presence of tetracyanoethylene. Thus complexes of trimethylenemethane may give the free compound. Photochemical degradation of the complex with iron tricarbonyl[36] yields a complicated mixture, containing the dimer *p*-xylene, paracyclophane, and several other products. In the presence of cyclopentene 2-methylenepentalene is formed by addition of the biradical to an isolated double bond. This type of addition has hitherto been regarded as impossible.

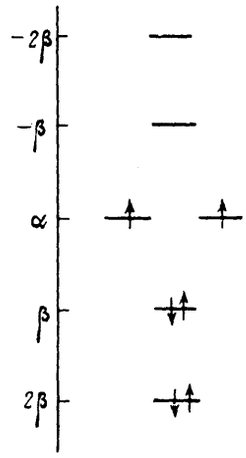
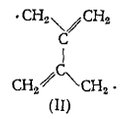


Figure 3. Energy-level diagram of the π-system of tetramethylene-ethane obtained by the Hückel molecular-orbital method.

3. Tetramethylene-ethane and its Complexes

Like trimethylenemethane, tetramethylene-ethane (II)



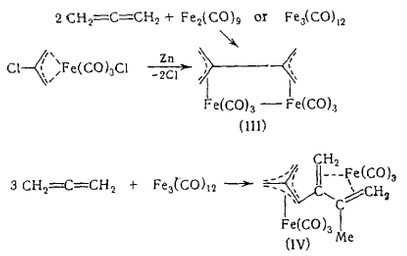
(II)

also has the triplet ground state predicted theoretically[1] and confirmed experimentally[37]. Calculation by the Hückel method gives the energy-level diagram for the π-system[38] illustrated in Fig. 3. The delocalisation energy is respectively ~2 β and 0.35 β relative to the system with two double bonds and two localised electrons and relative to two allyl radicals. This species is comparatively

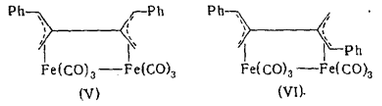
unstable in the free state, its lifetime at −196°C being about 20 min[37]. The formation of tetramethylene-ethane was suggested in a study of the degenerate thermal rearrangement of 1,2-dimethylenecyclobutane[39,40]. Tetramethylene-ethane is the central fragment of the stable bisgalvinoxyl biradical[41]. Electron spin resonance spectra have been obtained for the radical anion[42] and the radical cation[41] of tetramethylene-ethane.

The hypothesis that tetramethylene-ethane is an intermediate species in the di- and tri-merisation of allene was confirmed by isolation of the binuclear complexes (III) [43-46] and (IV) [47] in the reaction of allene with iron carbonyl (Scheme 2). The latter contains a ligand which is a kind of combination of trimethylenemethane and a tetramethylene-ethane derivative. The complex (III) can be obtained independently by eliminating the two halogen atoms from tricarbonyl-2-chloroallyliron chloride.

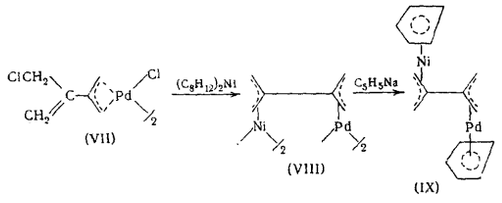
Scheme 2



Analogous complexes (V) and (VI) are obtained from phenylallene and iron carbonyl[48]. They are assumed to be isomeric, with different relative orientations of the substituents in the allyl groups

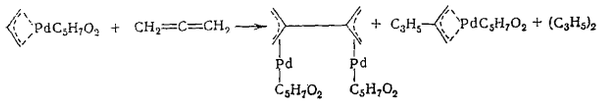


In the presence of palladium salts allene yields the complex (VII) together with other products[49-53]. If the reaction is conducted in a polar medium with excess of allene present, (VII) is the main product. The substituent in the allyl ligand of (VII) is itself a potential ligand. In fact it combines with an additional metal atom to give the tetramethylene-ethane complex (VIII),[54] which is capable of the usual reactions, e.g. rupture of the bridge by the action of C_5H_5Na:

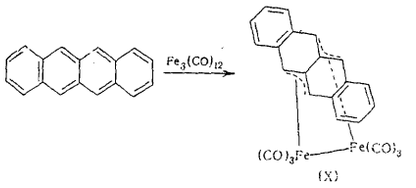


In time the complex (IX) thus formed disproportionates to give a derivative of the same metal, viz. nickel. The transoid configuration of (IX) was supported by preliminary X-ray diffraction results[54].

An analogue of (VIII) can be obtained by the incorporation of allene into an existing π-allylic type of palladium complex with an acetylacetonate group[55]:



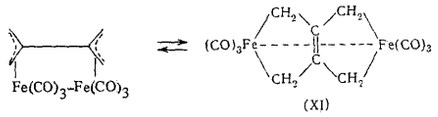
Finally, another surprising change to a tetramethylene-ethane derivative was discovered by Fischer et al.[56] When tetracene was heated with $Fe_3(CO)_{12}$, an extraordinarily stable compound containing two tricarbonyliron groups was formed, whose infrared and n.m.r. spectra suggested the structure (X):



Most complexes of tetramethylene-ethane are solids having surprising thermal stability. Their mass spectra contain peaks due to molecular ions[48].

Unfortunately there is as yet no single completed X-ray structural investigation of tetramethylene-ethane complexes. All the latter that have been described are binuclear compounds. This ligand probably cannot be coordinated other than with a few metal atoms without strong disruption of coplanarity and delocalisation. It would therefore be interesting to ascertain in what measure its fragments bound to different metal atoms are autonomous and whether the system preserves its planarity. Existing spectroscopic data seem to indicate that the two allylic systems are autonomous when the molecule contains two different metals. The n.m.r. spectrum of (IX) contains two sets of signals for each moiety of the molecule, as if each were independent. The *syn*- and *anti*-protons of each allylic group and the protons of the cyclopentadienyl rings absorb at different magnetic field intensities, and all signals for the nickel-containing moiety are displaced to a higher range than those for the moiety containing palladium.

The complex (III) possesses the properties of flexible systems. This is apparent in the variation of its spectrum with temperature and is explained[45] by a valency-tautomeric equilibrium of the type



The introduction of phenyl substituents raises the barrier to the dynamic process, and the spectra of (V) and (VI) show no dependence on temperature[47]. A third product was isolated in the preparation of complexes (V) and (VI); its spectral properties were compatible with structure (XI), and it underwent thermal rearrangement to (VI). Thus the possibility of valency tautomerism seems to be confirmed by isolation of a second equilibrium form. However, the molecules are quite complicated, and X-ray examination is very necessary to confirm these conclusions.

Complex (X) would also be interesting to examine by X-ray diffraction. The central portion of this molecule is quite analogous to (III), and the changes in the n.m.r. spectrum of tetracene after coordination are consistent with such a form of bonding. Further confirmation of the structure can be found in the infrared spectra, for carbonyl-containing complexes of iron have entirely analogous spectra in the region of carbonyl-stretching vibrations[48,56]. These workers give three bands for each of the two tricarbonyliron groups in (III), (V), and (VI)—e.g. at 2062, 2030, 1996, 1983, 1970, and 1940 cm^{-1} in the case of

(VI)—but the lower three bands are significantly less intense and are poorly resolved. The spectrum of complex (X) contains five bands, situated close to the first five bands enumerated above.

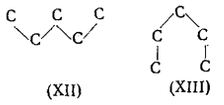
Chemical investigations of tetramethylene-ethane complexes are very sparse. These complexes are decomposed by bromine with the formation of 1,4-dibromo-2,3-bisbromomethylbut-2-ene[44,45].

III. COMPLEXES OF PENTADIENYL

A considerable number of complexes have now been prepared in which the transition metal is bound to an open chain of five unsaturated carbon atoms. These complexes can be combined under the name *pentadienyl*, although they can probably include structural variants. They have been known for about a decade, but only recently have they begun to be investigated systematically as a class.

1. Structural Characteristics of the Cation and Anion of Pentadienyl and the Pentadienyl Ligand

The simplest acyclic pentadienyl species (anion, cation, and radical) probably have the form (XII) of carbon skeleton. However, when this system is part of a ring of moderate size, (XIII) will be the more probable form of skeleton.

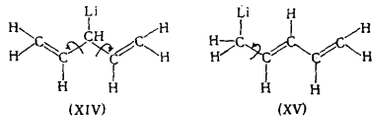


(XII) (XIII)

Fig. 4 shows the energy-level diagram of the π-system of pentadienyl. The delocalisation energy for all three species is 1.464 β.[2]

Acyclic dienyl cations are quite stable in strongly acid media, and can be observed directly by nuclear magnetic resonance[58]. At room temperature the molecules studied do not exhibit the properties of flexible systems.

The temperature variation of the n.m.r. spectrum of the pentadienyl anion (as the lithium derivative) indicates that the terminal protons become equivalent above 30°C.[59] This was explained by equilibrium between ionic and covalent forms of the lithium derivative, for which the two structures



(XIV) (XV)

were possible. Rotation about the single bond leads to interchange of the positions of the terminal protons. The spectral data show that rotation occurs more readily about inner than outer carbon — carbon bonds.

The chemical shifts for the various protons in the pentadienyl system suggest that the charge is distributed non-uniformly along the chain. In the anion the greatest electron density is concentrated on the odd carbon atoms, as predicted by theory[2,60].

Pentadienyl anions are capable of [1,6] sigmatropic rearrangements, which conform to the Woodward — Hoffman rules. These changes are slowed down by the presence of alkyl substituents[61].

The large majority of pentadienyl complexes known at the present time contain the ligand in the form (XIII), which is probably geometrically more favourable for coordination with a single metal atom. The only example in which form (XII) of pentadienyl is fixed on a transition metal is a bis-π-allylic type of nickel complex containing two metal atoms (see below).

Benzenonium ions are stabilised as pentadienyl complexes of transition metals. Almost all known complexes with this ligand in either form (around 150 individuals have been isolated) are quite stable compounds. The following experimental results enable the relative stability of the pentadienyl cation and its complexes to be compared with other cations and complexes of other ligands.

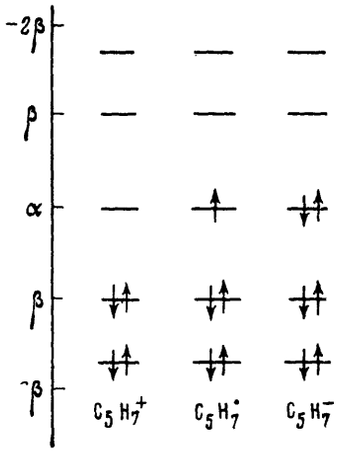
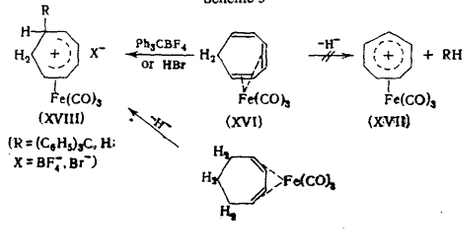


Figure 4. Energy-level diagram of the π-system of pentadienyl obtained by the Hückel molecular-orbital method.

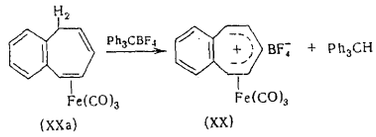
The cycloheptatriene derivative of iron (XVI) has one free double bond and an α-methylene group relative to the coordinated system (Scheme 3). However, it exhibits no tendency to change into the tropylium complex (XVII) under conditions such that a hydride ion is usually easily detached from an α-methylene group[62-64].

Scheme 3



Scheme 3 shows that (XVI) develops acceptor properties towards electophiles: it adds a proton or a triphenylmethyl cation to give the complex (XVIII) with a pentadienyl ligand[62,65]. On the other hand, the same cation and its analogue (XX) [66] can be obtained in the usual way—by

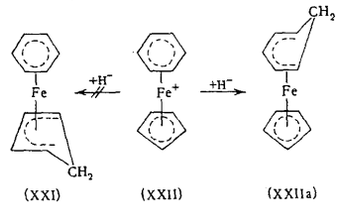
detachment of a hydride ion from (XIX) and (XXa) respectively:



(XXa) (XX)

The n.m.r. spectrum of (XX) shows that the positive charge is mainly localised in the pentadienyl system, and is not transmitted to the benzene ring: i.e. the coordinated form (XX) is probably correct, not the alternative benzotropylium form. The formation of pentadienyl complexes by the detachment of a hydride or a hydroxide[67] ion under the influence of a triphenylmethyl salt suggests that the resulting complex cations are more stable (less electrophilic) than the triphenylmethyl cation, whereas the reverse order of stability is observed for the free species. Thus the diminution in electrophilicity on passing from $C_6H_7^+$ to $C_6H_7Fe(CO)_3^+$ obviously results from the transmission of electron density from the tricarbonylmethyl group. The pentadienyl cation is preferable to the tropylium cation for iron, primarily because it is a four-electron donor. A vast quantity of experimental results confirm the special affinity of iron for organic ligands, contributing four electrons to the common electron shell. Furthermore, the pentadienyl cation contains a vacant non-bonding π-orbital, more capable than the antibonding orbital of the tropylium cation of taking part in dative bonding[2,38].

Having studied the reduction of a large number of arene-ironcyclopentadienyl (XXII) salts by hydride reductants[68-70], and also the addition to them of other nucleophilic reagents[71], Pauson and his coworkers showed convincingly that only the six-membered ligand changes, and of the two possible products (XXI) and (XXIIa) only the latter is obtained:



(XXI) (XXII) (XXIIa)

This probably applies also to the cathodic reduction of these salts[72].

Similarly, six- and seven-membered (but not four-membered) ligands add a hydride ion on the reduction of $C_7H_8CoC_4R_4^+$ and $C_6H_6CoC_4R_4^+$:[73,74] in other words, the pentadienyl ligand is preferred to the butadiene and allyl ligand respectively.

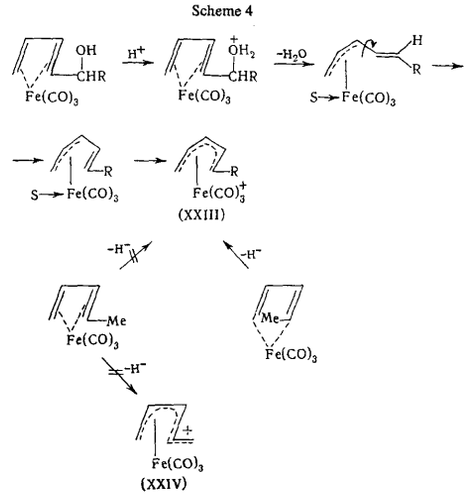
The structural problems discussed below are being studied in connection with pentadienyl complexes.

(*a*) *cis*- and *trans*-Forms of the ligand

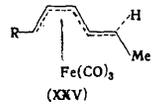
When this ligand does not form part of a ring, it may be expected (in view of the geometry of the initial diene complexes) that *cis*- and *trans*-forms—(XXIII) and (XXIV)—will be produced. Pentadienyl derivatives of this kind are usually obtained from substituted diene complexes by the detachment of an anion from a side-chain[75-77] (Scheme 4).

An immense quantity of experimental results shows that, independently of the initial configuration, either the *cis*-form of the complex is obtained or else the reaction does not take place at all (Scheme 4). The mechanism of inversion[76] is clear from the scheme, and involves complexes of allylic type at intermediate stages.

Scheme 4



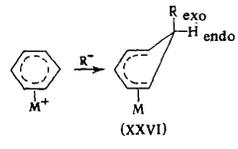
Recent spectral[78-80] and chemical[81,82] results indicate that a complex can be obtained with a ligand in the *trans*-configuration. The temperature dependence of the n.m.r. spectrum of acid solutions of tricarbonyl(2-methylhepta-3,5-dien-2-ol)iron and analogous compounds[79] shows that the *trans*-isomer exists in solution at temperatures below −50°C. The activation energy of conversion to the *cis*-form is ~13 kcal mole^{-1}. Preservation of the *trans*-configuration of the cation at low temperatures was attributed[80] to vertical stabilisation of the ionic centre by iron:



(XXV)

(*b*) Steric configuration of the ligand

The next problem, whose solution required considerable effort, involved the stereochemistry of the addition of nucleophiles (and thus the three-dimensional structure of the complexes) in the conversion of arene-containing complex cations into neutral cyclohexadienyl complexes:



(XXVI)

Spectral[68-71] and X-ray diffraction[83] results suggest that nucleophilic species (H^-, $C_6H_5^-$, CH_3^-) add on the outside of the ligand, and the ingoing substituent occupies an *exo*-position. This destroys the coplanarity of the ring, and the cyclohexadienyl ligands assume the form (XXVI). It

will be shown below that seven-membered rings buckle similarly.

The infrared spectra of cyclohexadienyl complexes have one extremely interesting feature: they contain an unusually low carbon — hydrogen stretching band (2730 — 2830 cm^{-1}),[71] which seems to be independent of the nature of the metal. Recent structural investigations show that this band is undoubtedly due to the *exo*-proton of the methylene group. The lowering of the frequency is no doubt caused by complex formation, since the free hydrocarbons do not exhibit anomalous bands. Because of the geometry of cyclohexadienyl complexes, illustrated above and to be discussed in detail later, it can hardly be supposed that the methylene *exo*-proton will interact through a tetrahedral carbon atom with the electron system of the metal[84]. Hyperconjugation is assumed to be possible in a molecule of the complex[71], as a consequence of overlapping of the σ-bonding *exo*-hydrogen — carbon orbital and neighbouring π-orbitals of the ligand directly involved in combining with the metal. The displacement of electrons from the carbon — hydrogen bond resulting from such interaction lowers the frequency of the stretching vibration. Experimental and calculated results[71] show that this phenomenon is general in character for ligands formed from five- and seven-membered rings. The cation $C_6H_7Fe(CO)_3^+$ is an exception to the general rule: its spectrum contains no anomalous band[84,85].

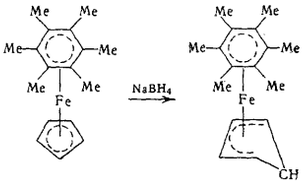
The nuclear magnetic resonance data[71] indicate that atoms and groups (hydrogen, methyl, phenyl) occupying an *exo*-position with respect to the metal are more strongly shielded than the corresponding *endo*-substituents: i.e. *endo*- and *exo*-substituents differ in their n.m.r. spectra. Protons and substituents situated in the coordinated moiety also exhibit non-equivalence, and the order of variation in shielding is opposite to that for benzenonium ions[68]. We shall return to this fact later.

Stereospecificity of addition to a complex cation may be due to spatial requirements or to an unsymmetrical distribution of electron density with respect to the plane of the ligand in the initial molecule, involving concentration on the *endo*-side, i.e. closer to the metal. Hence the approach of an anion will occur preferentially on the *exo*-side.

The direction of attack by a nucleophile on substituted arene complexes is determined to some extent by the nature of the substituents. A hydride ion usually goes towards an unsubstituted carbon atom in the benzene ring; when the number of such sites is small ($n < 3$), addition occurs also at a substituted carbon atom. When R = CH_3 ($n = 1 - 3$), the reaction involves almost exclusively unsaturated positions with a random probability distribution[68]. If methoxyl is the substituent, reduction occurs predominantly *meta* thereto. In the reduction of $CH_3OC_6H_5FeC_5H_5$, for example, the relative reactivities of the positions were found to be $o:m:p = 1:5:3$.[69] This may be due to a decrease in the local positive charge at the *ortho* and *para* positions owing to $p_\pi - p_\pi$ overlapping of the π-system of the ring and a lone pair on the oxygen.

When the nuclear substituent is a halogen, reduction occurs mainly in the *ortho* position, probably owing to the electron-accepting inductive effect of the halogen.

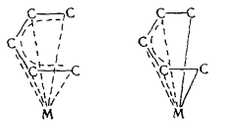
The addition of anions—$C_6H_5^-$, CH_3^-,[71,86] etc.—is in general controlled by the same rules. For example, the reaction between $CH_3C_6H_5FeC_5H_5^+$ and methyl-lithium involves unsubstituted carbon atoms, and *ortho*, *meta*, and *para* positions are equally reactive[71]. Only when all hydrogen atoms of the six-membered ring have been substituted does the behaviour of the cation on reduction change significantly: hexamethylbenzeneironcyclopentadienyl is reduced by adding a hydride ion to the five-membered ring[71]:



Similarly, only $C_6H_7MnC_6(CH_3)_6$ is obtained[87] of the two possible reduction products of the cation $C_6H_6MnC_6(CH_3)_6^+$.

(c) Possible forms of bonding with metal

The distribution of electron density in the pentadienyl ligand is of great interest. It is important to elucidate whether there is equivalent bonding of all five carbon atoms with the metal as in (XXVII) or whether the terminal carbon atoms are bound to the metal by σ-bonds, while the central portion acts as a π-allyl (structure XXVIII):



(XXVII) (XXVIII)

The latter suggestion is based on the above mentioned non-coplanarity of the rings, which may be due to rehybridisation at the terminal atoms of the coordinated portion.

Several structural investigations have been made on pentadienyl complexes, but all on derivatives in which this ligand forms part of a ring. Thus more or less complete investigations have been made on $C_6H_7Mn(CO)_3$,[84] azulene — $Mn_2(CO)_6$,[89,90] $(CH_3)_6C_6HRe(CO)_3$,[83] two azulene complexes of molybdenum carbonyl[91-93], and μ-(ππ-1, 6-dihydroheptalenebistricarbonylmolybdenum)[94]. Figs. 5 and 6 illustrate results obtained by Churchill and his coworkers for $C_6H_7Mn(CO)_3$ and guaiazulene — $Mo_2(CO)_6$ [84,93] derivatives of cyclohexadienyl and cycloheptadienyl respectively. The main features of these structures are easily seen. As already noted, the tetrahedral carbon atom in the cyclohexadienyl complexes is deflected substantially (by 42°) from the plane formed by the remaining five carbon atoms, which are arranged almost in the same plane and form an open pentagon. In $(CH_3)_6C_6HRe(CO)_3$ the deflection of the methylene group reaches 50°.[83] The deflection in structures analogous to Fig. 6 is considerably smaller (10 — 18°), which may be due to the presence of a direct metal — metal bond or of a second carbonylmetal group[90].

Like the other examples studied, the structures also show some lack of symmetry in the situation of the metal relative to the pentadienyl fragment, although the carbon — carbon bonds remain the same (~1.40 Å). As in the π-allylic complexes the metal is located closest to the central carbon atom of the system; the distances to the terminal and intermediate carbon atoms are 0.2 — 0.07 Å longer. The distances to the remaining carbon atoms, not directly bound to the metal, increase still more (difference up to 0.5 Å). The carbon — carbon distances are rather shorter in the pentadienyl than in the cyclopentadienyl ligand, while the mean metal — carbon distances are longer. This indicates stronger bonding of the metal

to the cyclopentadienyl than to the pentadienyl ligand, or else stronger bonding inside the pentadienyl than in the cyclopentadienyl fragment.

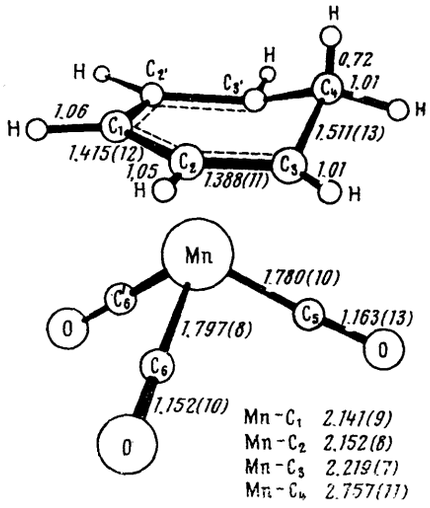


Figure 5. Structure of tricarbonyl(cyclohexadienyl)manganese[84].

The $C_{(4)}-C_{(3)}$ and $C_{(4)}-C_{(3')}$ bonds (Fig. 5) and the $C_{(4)}-C_{(10)}$ and $C_{(8)}-C_{(9)}$ bonds (Fig. 6) are elongated, and approach values corresponding $C_{sp^2}-C_{sp^3}$ bonds.

The angles in the cyclopentadienyl ring are rather smaller than the ideal angles for sp^2- and sp^3-hybridised carbon. All the azulene complexes studied exhibit shortening of the $C_{(9)}-C_{(10)}$ distances and lengthening of the $C_{(4)}-C_{(10)}$ and $C_{(8)}-C_{(9)}$ distances relative to uncoordinated hydrocarbon, which indicates that the two systems of π-electrons in the coordinated hydrocarbon are largely autonomous.

Thus the metal – carbon distances show rather weaker bonding between the terminal atoms of the pentadienyl system and the metal than with the central part of this ligand. However, no significant alternation in carbon – carbon bond lengths is observed, so that there are at present no grounds for discussing the limiting structure (XXVIII). On the other hand, the n.m.r. spectra also indicate an unsymmetrical distribution of electron density along this fragment. In fact, signals from protons attached to the terminal carbon atoms are observed at significantly higher fields than those from protons attached to the central carbon atoms of the system. With $C_6H_7MnC_6(CH_3)_6$, for example, we have the values (in ppm)—*exo*-H 1.05, *endo*-H and $H_{(3,3')}$ 1.4, $H_{(2,2')}$ 3.5, and $H_{(1)}$ 5.0 [87]—and a similar rule is observed for cycloheptadienyl complexes[88]. Furthermore, the chemical shifts depend on the nature of the solvent[95], which may be due to differences in electron density at different positions in the ligand. A final conclusion on the degree of asymmetry of bonding will obviously become possible after further structural investigations by both spectral and X-ray methods.

The first indications have been obtained that certain π-cyclohexadienyl systems are flexible[86]. However, the nature of the dynamic processes underlying such behaviour remains obscure.

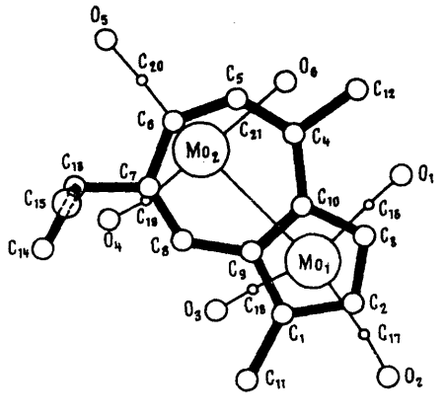


Figure 6. Structure of complex of guaiazulene with $Mo_2(CO)_6$.[93]

2. Methods of Preparation of Pentadienyl Complexes

We shall mention some general methods of preparation of pentadienyl complexes, in addition to those considered above.

1. Direct reaction between alkali-metal pentadienyl derivatives and salts of transition metals. Such a reaction has as yet been accomplished only in a single example with chromium(II) chloride[96]:

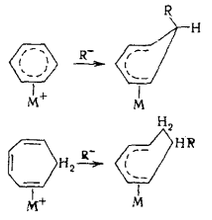
$$CrCl_2 + 2\,NaC_5H_7 \xrightarrow[-30^\circ C]{\text{oxolan}} Cr(C_5H_7)_2 + 2\,NaCl$$

The product of this reaction is very interesting. It exists as a monomer containing two pentadienyl groups and one chromium atom, is thermally stable (m.p. 122°C), and has two unpaired electrons. It resembles triallylchromium in its chemical properties: it is extremely sensitive to air, easily eliminates pentadiene on appropriate treatment, and is converted by carbon monoxide into $(C_5H_7)_2Cr(CO)_2$. No structural data are available, so that nothing definite can yet be said on the character of the bond.

Another complex of acyclic pentadienyl $(C_5H_7)_2Ni_2$ is now known, which contains two pentadienyl ligands and two metal atoms. This complex is obtained from nickel dichloride and penta-1,4-diene in the presence of triethylaluminium[97]. X-Ray results[98] show a di-π-allylic type of structure (Fig. 7). The nickel acquires its characteristic sixteen-electron shell, while the ligand is fixed in its most usual form.

2. Reduction of complex cations containing six- and seven-membered cyclic ligands. This method is used considerably more frequently[68-70,73,87,95,99-103]. Since the behaviour of the hydride anion and other nucleophilic agents is similar[71,86,88,99,104-107], this method may have even wider

application. It is suitable for the preparation of neutral cyclohexadienyl and cycloheptadienyl derivatives of all those metals for which the initial arene and cycloheptatriene complexes have been obtained:



(R = H, Alk, Ar, AlkO, CN, NR_2)

The reductants most often used are sodium tetrahydroborate, lithium tetrahydroaluminate, and sodium in liquid ammonia[102].

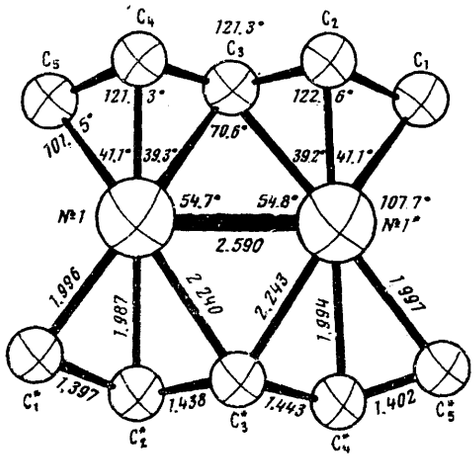


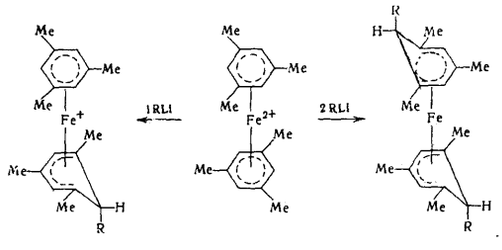
Figure 7. Structure of bispentadienyldinickel[98].

Several aspects of these reactions have been considered above. It should be added that the electronic requirements of the central atom also affect the course of these reactions. For example, reduction of the dibenzenerhenium and dibenzenetechnetium cations leads to the formation of benzenecyclohexadienyl complexes, whereas the doubly charged dibenzeneruthenium cation is reduced predominantly to benzenerutheniumcyclohexadiene[99]:

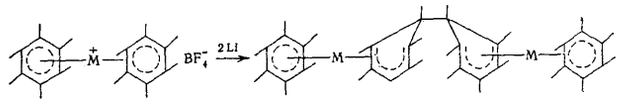
$$(C_6H_6)_2Ru^{2+} + NaBH_4 \rightarrow \underset{\text{main product}}{(C_6H_7)_2Ru} + C_6H_6RuC_6H_8$$

$$(C_6H_6)_2Re^{1+} + NaBH_4 \rightarrow C_6H_6ReC_6H_7$$

The corresponding cation of iron adds one or two moles of RLi:[86]

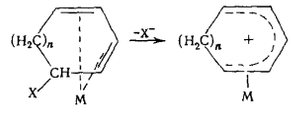


In isolated cases reduction is accomplished by an alkali metal alone, e.g. by fusing with metallic lithium[102,103]:



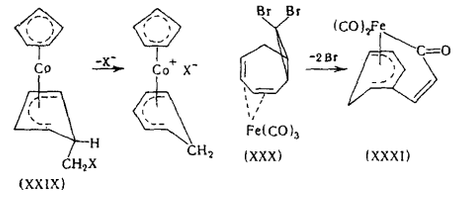
Reduction has been used to obtain all the known types of cyclohexadienyl complexes—$C_6H_7M(CO)_n$, $C_6H_7MC_5H_5$, $C_6H_7MC_6H_6$, $(C_6H_7)_2M$, $C_6H_7MC_4H_4$—in which this ligand is accompanied by carbonyl, cyclopentadienyl, arene, and cyclobutadiene ligands.

3. Detachment of an anion from an α-methylene of a diene complex. This method is suitable for obtaining cyclohexadienyl, cycloheptadienyl, and acyclic pentadienyl derivatives as cations[62,64,66,67,75-77,81,108]. The outgoing species may be hydride, methoxide, hydroxide, or halide ions. In contrast to the previous reactions, complex salts are formed here:



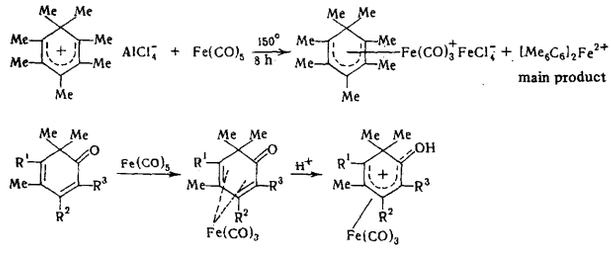
($n = 0, 1, 2$)

This method yields predominantly pentadienylcarbonyl complexes of general formula $C_5H_5[CH_2]_nM(CO)^+_m$. A proton or a triphenylmethyl cation may act as acceptor for the outgoing anions. These reactions are sometimes accompanied by enlargement[67,109-111] or contraction[112-114] of the rings. Solvolysis of (XXIX), for example, yields a cyclohexadienylcyclopentadienylcobalt cation (a cobalticinium analogue), and (XXXI) is obtained from (XXX) by treatment with methyl-lithium:

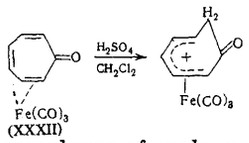


4. Addition of cations to free ethylenic group in polyalkene complexes. Salts of complex cations are obtained by the protonation of uncharged derivatives of diene type containing at least one free unsaturated group in the ligand[65,115-121] or by adding to it a carbonium ion[62,122], which has also received brief mention above. For example, complexes of bezenonium ions can be obtained by direct reaction with iron carbonyl[122] or by protonating a cyclohexadienone complex[120] (Scheme 5).

Scheme 5

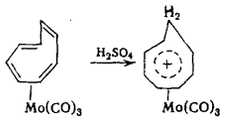


The cycloheptatrienone derivative (XXXII) is protonated at a carbon – carbon double bond[121]:

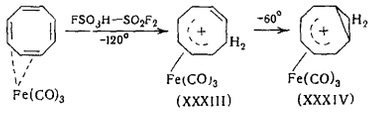


(XXXIII)

The protonation of complexes of cyclo-octatriene[119] and cyclo-octatetraene[115,117] provides a vivid example of how the electronic requirements of the metal determine the form of coordination of the organic cation. Thus the protonation of $C_8H_8Mo(CO)_3$ yields a homotropylium complex in which all six π-electrons of the ligand are involved in bonds with the metal[123]:



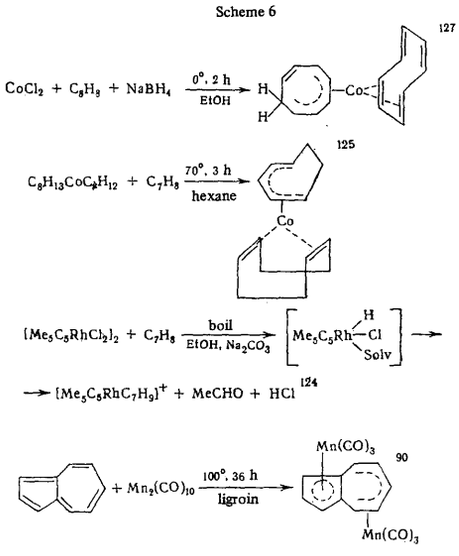
The protonation of $C_8H_8Fe(CO)_3$ [115,117] ultimately gives tricarbonyl(bicyclo[5,1,0]octadienyl)iron (XXXIV), where only four π-electrons of the pentadienyl system are used in bonding with iron:



The formation of (XXXIV) results[117] from electrocyclic ring closure in the coordinated organic ligand (XXXIII). The form of bonding in (XXXIII) is analogous to that for tricarbonyl(tropylium)iron[116].

5. Other modes of formation of pentadienyl derivatives. Pentadienyl complexes are formed in several cases of reaction between unsubstituted alkenes and various metal derivatives[90,124-128]. A few examples of such reactions are given below. The conversion of an alkene to a pentadienyl ligand requires the presence of metal hydrides, which may be introduced either directly[127] or may be formed in an intermediate stage of the process[124], the source of hydrogen being either the solvent or one of the components[125] (Scheme 6).

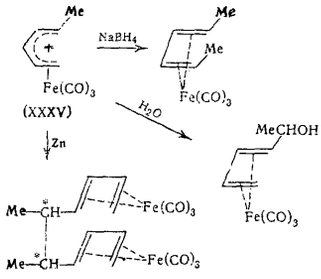
Scheme 6



3. Chemical Properties of Pentadienyl Complexes

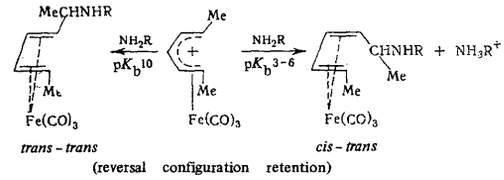
The above experimental results show that in most cases the formation of pentadienyl complexes is reversible. This does not mean that an equilibrium is established between the initial compound and the reaction product. Under suitable conditions, however, it is possible to effect the reverse change, and convert pentadienyl complexes into the diene complexes. Thus the complex (XXXV), obtained by detachment of a hydride ion from the corresponding diene complex, can be reduced by sodium tetrahydroborate[77], and also undergoes other reactions yielding diene complexes[129] (Scheme 7).

Scheme 7



The mechanisms of the reactions of complex cations with nucleophilic agents show specific differences, while conforming to general rules. For example, the reaction between $C_6H_7Ru(CO)_3^+$ and the methoxide anion begins with attack by the latter on the carbonyl group[130]. An intermediate product—the complex $C_6H_7Ru(CO)_2COOCH_3$ containing an ester group—was isolated, which gives the substituted diene complex $CH_3OC_6H_7Ru(CO)_3$ by rearrangement. However, in none of the other cases studied, those already mentioned and reported in Refs. 131 – 134, when the attacking species were nucleophiles from the hydride ion to amines, alkoxides, and β-diketones, was it possible to find any indication that the reaction followed a similar course or that the metal atom was attacked initially.

If the pentadienyl ligand does not form part of a ring, interaction with a nucleophile may involve either reversal or partial retention of the geometrical configuration of the ligand[76,77,133,134]. The geometrical form of the products obtained with amines depends on the basicity of the amine[133,134]:



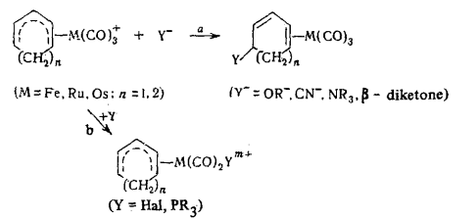
Addition is much slower when ligands possessing weaker acceptor properties than the carbonyl group are introduced into the initial complex. Increasing the size of the ring acts in the same direction: seven-membered ligands react more slowly than do six-membered ligands. The following sequence of reactivity has been found towards pentane-2,4-dione[132]:

$$C_6H_7Os(CO)_3^+ \simeq C_6H_7Fe(CO)_3^+ > C_6H_7Fe(CO)_2PPh_3^+ > C_7H_9Fe(CO)_3^+ > MeOC_6H_6Fe(CO)_3^+ \gg C_7H_9Fe(CO)_2I > C_7H_9Fe(CO)_2CN,\ MeOC_6H_6Fe(CO)_2I.$$

Neither β-diketones nor amines react with the later members of the series. All this suggests the probable occurrence of direct attack on the pentadienyl ligand.

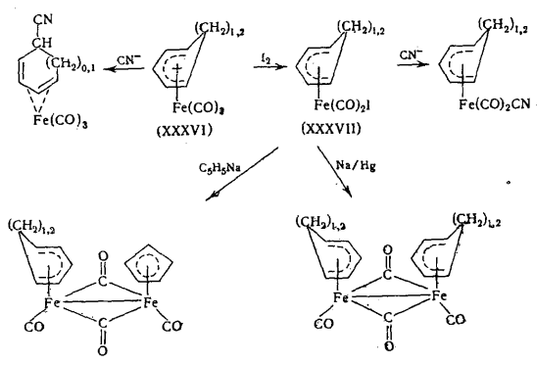
These reaction yield neutral complexes of substituted dienes (Scheme 8*a*). However, there are examples of a quite different course of reaction with nucleophiles, involving retention of the pentadienyl ligand and substitution of other groups present in the molecule (*b*).

Scheme 8

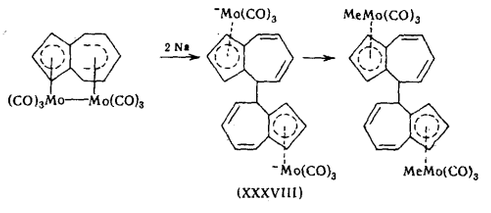


Pauson et al.[135] investigated the chemical reactions of pentadienyl derivatives of iron and compared them with those of aromatic cyclopentadienyl complexes. The cations (XXXVI: $n = 1, 2$) react with iodine, with replacement of one of the carbonyl groups and conversion into neutral compounds (XXXVII) having very similar properties to $C_5H_5Fe(CO)_2I$. These iodides are in fact able to exchange covalently bound halogen, and dimerise when reduced with sodium amalgam or treated with C_5H_5Na. This sometimes involves substitution of the pentadienyl ligand (Scheme 9). However, the above addition reactions with conversion into a diene system—quite uncharacteristic of aromatic complexes—are more characteristic of pentadienyl complexes. This constitutes their main chemical difference.

Scheme 9



When discussing the X-ray results we noted that a metal is more weakly bound to a pentadienyl than to a cyclopentadienyl ligand. This is suggested also by the formation of (XXXVIII) when the azulene complex of molybdenum carbonyl is treated with metallic sodium[93,136]:



Rupture of the molybdenum — molybdenum bond is accompanied also by cleavage of the bond with the seven-membered ring, i.e. with pentadienyl, whereas the bond with the five-membered ring is preserved.

Table 2 lists data for the complexes of pentadienyl with various metals.

Table 2. Summary of data on complexes with pentadienyl.

Metal	Compound	Colour	M.p., °C	Ref.
Ti	$C_7H_9TiC_7H_7$	green	cryst.	128
V	$C_6H_7V(CO)_4$	dark brown	66 (decomp.)	101
	1,2[a]-$Me_2C_6H_5V(CO)_4$	ditto	68 (decomp.)	101
	1,4[a]-$Me_2C_6H_5V(CO)_4$	»	—	101
	1,2,3[a]-$Me_3C_6H_4V(CO)_4$	»	73 (decomp.)	101
	1,2,4[a]-$Me_3C_6H_4V(CO)_4$	»	—	101
	1,3,5[a]-$Me_3C_6H_4V(CO)_4$	»	94 (decomp.)	101
	1,2,3,4[a]-$Me_3C_6H_5V(CO)_4$	»	75	101
	1,2,4,5[a]-$Me_4C_6H_3V(CO)_4$	»	74	101
	$Me_6C_6HV(CO)_4$	»	—	101
Cr	$(C_5H_7)_2Cr$	green	122	96
	$[(C_5H_7)_2CrCO]_2$	—	—	96
Mo	azulene-$Mo_2(CO)_6$	—	—	91, 92, 136, 137
	guaiazulene —$Mo_2(CO)_6$	—	—	91, 92
	1,6-dihydroheptalene —$Mo_2(CO)_6$	red	cryst.	94
Mn	$C_6H_7MnC_6Me_6$	red	120 (decomp.)	84
	$C_6H_7Mn(CO)_3$	yellow	78 (decomp.)	84, 95, 138
	X—$MeC_6H_6Mn(CO)_3$ (A)	yellow	liquid	95
	X—$MeC_6H_6Mn(CO)_3$ (B)	yellow–orange	liquid	95
	exo-4[c]-$MeC_6H_6Mn(CO)_3$	orange	90	104
	exo-4[c]-$CNC_6H_6Mn(CO)_3$	—	—	105
	$PhC_6H_6Mn(CO)_3$	yellow	112 (decomp.)	85, 99
	1,3,5[a]-$Me_3C_6H_4Mn(CO)_3$	orange	liquid	95
	4[b]-CN—1,3,5-$Me_3C_6H_3Mn(CO)_3$	white	109 (decomp.)	105
	exo-4[c]-CN—$Me_4C_6H_2Mn(CO)_3$	—	—	105
	$C_7H_9Mn(CO)_3$	yellow	66	88, 106
	4[b]-$MeC_7H_8Mn(CO)_3$	light yellow	39	88, 106
	4[b]-$PhC_7H_8Mn(CO)_3$	—	75	106
	4[b]-$CNC_7H_8Mn(CO)_3$	—	58	106
	4[b]-$MeOC_7H_8Mn(CO)_3$	yellow	61	88, 106
	4[b]-$EtOC_7H_8Mn(CO)_3$	—	40	106
	4[b]-t-$BuOC_7H_8Mn(CO)_3$	—	142	106
	4′, 4[b]-$C_7H_8Mn(CO)_3$—$OC_7H_8Mn(CO)_3$	light yellow	158	106
	4[b]-$Me_2NC_7H_8Mn(CO)_3$	—	38	106
	4[b]-$Me_3INC_7H_8Mn(CO)_3$	—	154 (decomp.)	106
	azulene —$Mn_2(CO)_6$	light yellow	cryst.	89, 90
	$C_{10}H_9Mn(CO)_3$	orange	10	95
	$C_7H_9Mn(CO)_2PPh_3$	yellow	110	106
Re	$C_6H_7ReC_6H_6$	orange-red	195	85, 99
	$Me_6C_6HReC_6Me_6$	orange-yellow	212 (decomp.)	102
	$Me_6C_6Re(C_6Me_6)_2ReC_6Me_6$	yellow	225 (decomp.)	102
	$Me_6C_6HRe(CO)_3$	golden	118 (decomp.)	83, 100
Tc	$C_6H_7TcC_6H_6$	yellow	178 (decomp.)	103
	$Me_6C_6HTcC_6Me_6$	yellow	235 (decomp.)	103
	$Me_6C_6Tc[C_6Me_6]_2TcC_6Me_6$	red	230 (decomp.)	103
Fe	$[PhC_6H_3Me_3]_2Fe$	orange	105	86
	[t-$BuC_6H_3Me_3]_2Fe$	orange	204	86
	$[CH_2{=}CHC_6H_3Me_3]_2Fe$	orange	132	86
	$C_6H_7FeC_5H_5$	orange–red	135	68, 72, 85, 99, 139
	exo-4[b]-$MeC_6H_6FeC_5H_5$	—	65/0, 005 mmHg	71

Table 2 (contd.)

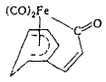
Metal	Compound	Colour	M.p., °C	Ref.
	$MeC_6H_6FeC_5H_5$[b]	—	37.70/0.005 mmHg	68
	exo-4[b]-$PhC_6H_6FeC_5H_5$	red	157	85, 99
	$MeOC_6H_6FeC_5H_5$[c]	—	55/0.005 mmHg	69
	2[b]-$ClC_6H_6FeC_5H_5$	—	72	70
	3[b]-$ClC_6H_6FeC_5H_5$	—	91	70
	3[b]-$BrC_6H_6FeC_5H_5$	—	98	70
	1,2[a]-$Me_3PhFeC_5H_5$[c]	—	65/0.005 mmHg	63, 68
	1,3[a]-$Me_2C_6H_5FeC_5H_5$[c]	—	50/0.005 mmHg	68
	1,4[a]-$Me_6C_6H_5FeC_5H_5$	—	45/0.005 mmHg	68
	1-Me-2[a]-$MeC_6H_5FeC_5H_5$[c]	—	45/0.005 mmHg	69
	1-Me-3[a]-$MeOC_6H_5FeC_5H_5$[c]	—	65/0.005 mmHg	69
	2[b]-Me-5$MeOC_6H_5FeC_5H_5$	—	50—51	69
	2,5[b]-$(MeO_2)C_6H_6FeC_5H_5$	—	47/0.005 mmHg	69
	3-Cl-5[b]-$MeC_6H_5FeC_5H_5$	—	viscous liquid	70
	3-Cl-1[b]-$MeC_6H_5FeC_5H_5$	—	viscous liquid	70, 71
	3-Cl-2[b]-$MeC_6H_5FeC_5H_5$	—	80	70
	5-Cl-2[b]-$MeC_6H_5FeC_5H_5$	—	73/0.005 mmHg	70
	2-Cl-5[b]-$MeC_6H_5FeC_5H_5$	—	viscous liquid	70
	1-Cl-3[a]-$MeOC_6H_5FeC_5H_5$[c]	—	58/0.005 mmHg	69
	3-Br-2[b]-$MeC_6H_5FeC_5H_5$	—	viscous liquid	70
	5-Br-3[b]-$MeC_6H_5FeC_5H_5$	—	viscous liquid	70
	5-Br-2[b]-$MeC_6H_5FeC_5H_5$	orange	61/0.005 mmHg	70
	2,3[b]-$Cl_2C_6H_5FeC_5H_5$	—	58	70
	1,2[b]-$Cl_2C_6H_5FeC_5H_5$	—	viscous liquid	70
	3,5[b]-$Cl_2C_6H_5FeC_5H_5$	—	84	70
	1,3[b]-$Cl_2C_6H_5FeC_5H_5$	—	viscous liquid	70
	2,6[b]-$Cl_2C_6H_5FeC_5H_5$	—	viscous liquid	70
	3,6[b]-$Cl_2C_6H_5FeC_5H_5$	—	39	70
	2-Br-5[b]-$MeC_6H_5FeC_5H_5$	orange	viscous liquid	70
	exo-4[b]-Me-2,5-$(Me_2)_2C_6H_4FeC_5H_5$	—	45/0.005 mmHg	71
	1,2,3[a]-$Me_3C_6H_4FeC_5H_5$[c]	—	32	68
	1,2,4[a]-$Me_3C_6H_4FeC_5H_5$[c]	—	—	68
	1,3,5[a]-$Me_3C_6H_4FeC_5H_5$	dark red	75/0.005 mmHg	68, 139
	exo-4[b]-Ph-2,5-$(Me_2)C_6H_4FeC_5H_5$	—	68	71
	2,6[a] - Me_2 - 1-$MeOC_6H_4FeC_5H_5$[c]	—	80/0.005 mmHg	69
	1,2,4,5[a]-$Me_4C_6H_3FeC_5H_5$[c]	—	55/0.005 mmHg	68
	exo-4[b]-Me-1,3,5-$Me_3C_6H_3FeC_5H_5$	—	39	71
	exo-4[b]-Ph-1,2,3-$Me_3C_6H_3FeC_5H_5$	—	99	71
	1,2,3,4,5[a]-$Me_5C_6H_2FeC_5H_5$[c]	—	viscous liquid	62
	exo-4[b]-Me-2,3,5,6-$Me_4C_6H_2FeC_5H_5$	—	60	71
	exo-4[b]-Ph-2,3,5,6-$Me_4C_6H_2FeC_5H_5$	—	90	71
	exo-4[b]-Me-1,2,3,5,6-$Me_5C_6HFeC_5H_5$	—	69	71
	$C_6H_7Fe(CO)_2CN$	yellow	91 (decomp.)	135
	$C_6H_7Fe(CO)_2I$	red-brown	96	135
	$[C_6H_7Fe(CO)_2]_2$	red	blackens 160	135
	$C_6H_7Fe(CO)_2Fe(CO)_2C_5H_5$	—	—	135
		yellow-orange	102	112—114
	$C_7H_9Fe(CO)_2I$	brown	99	132, 135
	$C_7H_9Fe(CO)_2CN$	orange	76 (decomp.)	132, 135
	$[C_7H_9Fe(CO)_2]_2$	red	198	135
	$C_7H_9Fe(CO)_2Fe(CO)_2C_5H_5$	red-brown	170	135
	$PhC_6H_3Me_3FeC_6H_3Me_3^+PF_6^-$	brown	217 (decomp.)	86
	t-Bu-$C_6H_3Me_3FeC_6H_3Me_3^+PF_6$	yellow-brown	238 (decomp.)	86
	$CH_2=CHC_6H_3Me_3FeC_6H_3Me_3^+PF_6^-$	yellow-brown	195 (decomp.)	86

Table 2 (contd.)

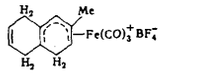
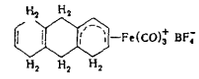
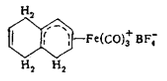
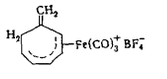
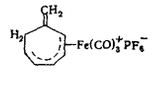
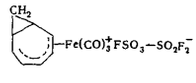
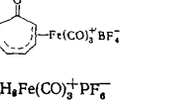
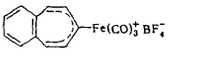
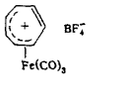
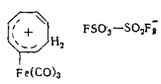
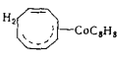
Metal	Compound	Colour	M.p., °C	Ref.
	$C_5H_7Fe(CO)_3^+ClO_4^-$	yellow	cryst.	76
	$C_5H_7Fe(CO)_3^+BF_4^-$	yellow	cryst.	76, 133
	sym-1-Me-$C_6H_6Fe(CO)_3^+ClO_4^-$	yellow	cryst.	75, 77
	sym-1-Me-$C_6H_6Fe(CO)_3^+BF_4^-$	yellow	195 (decomp.)	77
	sym, sym-1.5-$Me_2C_6H_5Fe(CO)_3^+BF_4^-$	yellow	220 (decomp.)	76, 133, 134
	$C_6H_7Fe(CO)_3^+BF_4^-$	light yellow	193 (decomp.)	63, 85, 132, 135
	$C_6H_7Fe(CO)_3^+PF_6^-$	—	—	108, 118
	1[b]-$MeC_6H_6Fe(CO)_3^+PF_6^-$	—	—	118
	2[b]-$MeC_6H_6Fe(CO)_3^+PF_6^-$	yellow	cryst.	64, 118
	2[b]-$MeC_6H_6Fe(CO)_3^+BF_4^-$	yellow	cryst.	64
	2[b]-$MeOC_6H_6Fe(CO)_3^+BF_4^-$	yellow	202 (decomp.)	64, 132
	3[b]-$MeOC_6H_6Fe(CO)_3^+PF_4^-$	yellow	—	64
	2-Me-5[b]-$MePhOFe(CO)_3^+BF_4^-$	—	—	64
	2-Me-5[a]-$MePhOFe(CO)_3^+BF_4^-$	yellow	124	64
		yellow	cryst.	64
		—	cryst.	64
	3-HO-1,4[b]-$Me_2C_6H_4Fe(CO)_3^+Al_2Cl_7^-$	—	—	120
	3-HO-2,4[b]-$Me_2C_6H_4Fe(CO)_3^+Al_2Cl_7^-$	—	—	120
		—	cryst.	64
	3-HO-1,2,4-Me_3-1[c]-$CD_3C_6H_2Fe(CO)_3^+Al_2Cl_7^-$	—	—	120
	3-HO-2,4,6-Me_3-1[b]-$CD_3C_6H_2Fe(CO)_3^+Al_2Cl_7^-$	—	—	120
	$Me_7C_6Fe(CO)_3^+FeCl_4^-$	yellow	cryst.	122
	$C_7H_9Fe(CO)_3^+Br^-$	light yellow	cryst.	65
	$C_7H_9Fe(CO)_3^+FeCl_4^-$	yellow	cryst.	65
	$C_7H_9Fe(CO)_3^+BF_4^-$	orange-red	>200 (decomp.)	62, 132, 135
	$C_7H_9Fe(CO)_3^+BPh_4$	light yellow	>240 (decomp.)	135
	$C_7H_9Fe(CO)_3^+ClO_4^-$	light orange	explodes 160	135
	$Ph_3CC_7H_8Fe(CO)_3^+BF_4^-$	light yellow	>100 (decomp.)	62
		—	cryst.	129
		—	cryst.	129
		—	—	112, 117
		—	140 (decomp.)	121
	4[b]-$MeOC_7H_8Fe(CO)_3^+PF_6^-$	—	cryst.	129
	3[b]-$MeOCOC_7H_8Fe(CO)_3^+BF_4^-$	—	—	67
	3[b]-$MeCOOCH_2C_7H_8Fe(CO)_3^+BF_4^-$	—	—	67
		yellow	230 (decomp.)	66
		yellow	112 (decomp.)	116

Table 2 (contd.)

Metal	Compound	Colour	M.p., °C	Ref.
		—	—	117
	$C_8H_7Fe(CO)_2PPh_3^+BF_4^-$	—	—	132
Ru	$(C_6H_7)_2Ru$	yellow	cryst.	85
	$Ph(C_6H_6)_2Ru$	yellow	158	85
	$C_8H_7Ru(CO)_3^+BF_4^-$	—	—	130
Co	$C_8H_7CoC_4Ph_4$	red	135	73, 74
	$C_7H_9CoC_4Ph_4$	dark red	188	73, 74
	4[b]-$BuC_6H_6CoC_4Ph_4$	orange-red	140	74
	4[b]-$BuC_6H_6CoC_4(C_6H_4Me)_4$	—	131	74
	$C_7H_9CoC_4Ph_4$	dark red	188	73, 74
	4[b]-$HOC_7H_8CoC_4Ph_4$	—	137 (decomp.)	74
	4[b]-$MeOC_7H_8CoC_4Ph_4$	orange-red	195 (decomp.)	74
	4[b]-$MeOC_7H_8CoC_4(C_6H_4Me)_4$	—	178 (decomp.)	74
	$C_7H_9CoC_8H_{12}$	red-brown	65 (decomp.)	125, 126
	$C_7H_9Co(CO)_2$	dark red	0—5	125
		black	95 (decomp.)	127
	$C_8H_7CoC_5H_5^+I^-$	red	110 (decomp.)	109, 111, 131
	$C_8H_7CoC_5H_5^+PF_6^-$	red	180 (decomp.)	109, 111, 131
	endo-4[b]-$MeC_8H_6CoC_5H_5^+PF_6^-$	—	160 (decomp.)	110
	endo-4[b]-$PhC_8H_6CoC_5H_5^+PF_6^-$	—	125 (decomp.)	110
	4,4[b]-$Me_2C_8H_5CoC_5H_5^+PF_6^-$	—	167 (decomp.)	110
	4,4[b]-$Ph_2C_8H_5CoC_5H_5^+PF_6^-$	orange	264 (decomp.)	110
Rh	$C_7H_9RhC_5Me_5^+Cl^-$	yellow	189 (decomp.)	124
	$C_7H_9RhC_5Me_5^+PF_6^-$	yellow	>260 (decomp.)	124
	$C_8H_{11}RhC_5H_5^+PF_6^-$	yellow	—	119
Ir	$C_7H_9IrC_5Me_5^+PF_6^-$	—	—	124

(a) Positions of substituents in initial hydrocarbon.

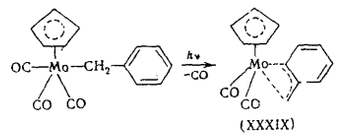
(b) Numbering as in  and 

(c) Mixture of isomers.

IV. THE BENZYL LIGAND IN TRANSITION-METAL COMPLEXES

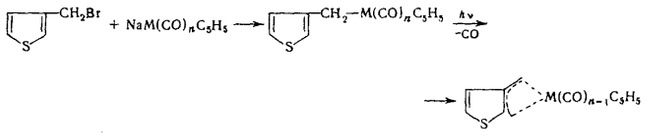
Comparatively recently a new form of coordination of aromatic molecules with transition metals—a π-allylic type of bonding involving one double bond of the benzene ring—has been discovered experimentally, and the products have been termed π-benzyl complexes.

King and Fronzaglia found that the products of prolonged ultraviolet irradiation of the σ-benzyl derivative of tricarbonyl(cyclopentadienyl)molybdenum included a small quantity of a substance containing one fewer carbonyl group than the starting material[140]:



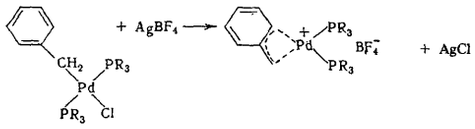
(XXXIX)

The structure (XXXIX) was suggested, and subsequently confirmed by X-ray diffraction. The same method has been used to obtain a few molybdenum and tungsten complexes substituted in the ligand[141,142] and also π-thienyl derivatives of molybdenum and iron[143]:



(M = Mo, Fe; n = 3, 2)

Complex cations in which a π-benzyl ligand is attached to palladium are obtained by a similar method[144]:



Thus in all these reactions an ethylenic group of the benzene ring occupies the coordination site vacated by the outgoing ligand. Compounds of this type that have been reported are quite stable, as indicated by their thermal constants (Table 3) and also the conditions of their preparation. In solution these complexes are unstable.

Table 3. Summary of data on complexes of π-benzyl type.

Metal	Compound	Colour	M.p., °C	Ref.
Mo	$PhCH_2Mo(CO)_2C_5H_5$	dark red	85	140
	4-$MeC_6H_4CH_2Mo(CO)_2C_5H_5$	red-orange	100	141, 142
	3,5-(i-$C_3H_7)_2C_6H_3CH_2Mo(CO)_2C_5H_5$	dark red	71	142
	β-$C_4H_3SCH_2Mo(CO)_2C_5H_5$	red-orange	127	143
	α-$C_4H_3SCH_2Mo(CO)_2C_5H_5$	red-orange	103	143
W	4-$MeC_6H_4CH_2W(CO)_2C_5H_5$	orange	127	142
Fe	β-$C_4H_3SCH_2Fe(CO)C_5H_5$	red	cryst.	143
Pd	$PhCH_2Pd(PEt_3)_2^+BF_4^-$	light yellow	cryst.	144
	2-Cl-$C_6H_4CH_2CHPd(PEt_3)_2^+BF_4^-$	yellow-orange	cryst.	144

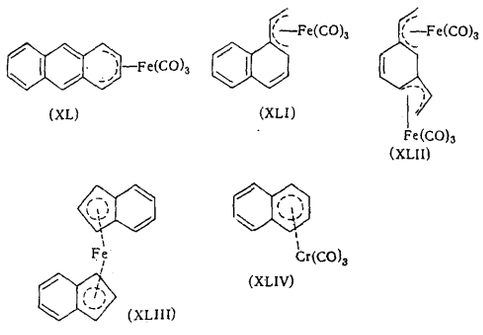
π-Benzyl complexes are easily obtained with molybdenum and tungsten, but not so well with iron. The yields of (XXXIX) and its analogues reach 25%, but the photochemical reaction of $C_5H_5Fe(CO)_2CH_2C_6H_5$ [145] involves elimination of the benzyl radical (not carbonyl) and dimerisation of the residue. The yields of thienyl derivatives of molybdenum amount to 30 — 50%, and of iron about 2% with poor reproducibility. However, the mass spectrum of $C_6F_5CF_2Fe(CO)_2C_5H_5$ includes a fragment corresponding to a π-benzyl derivative[146].

It is of considerable interest that the benzyl group can act as a bidentate ligand in complex formation. With such

coordination disturbance of the usual state of the molecule may be expected from that of delocalisation and the appearance of non-equivalence in the ethylenic groups of the ring. Therefore coordination of individual portions of an aromatic molecule would probably be determined by the donor — acceptor properties of such fragments and the metal-containing group of the complex. The very possibility of this type of interaction is being ascertained at the present time, and the first structural investigations have started.

Complexes of fused aromatic hydrocarbons have been reported, in which only part of the initial molecule is directly bound to the metal. They are represented (Scheme 10) by the structures (XL),[147] (XLI),[147] (XLII),[148] (XLIII),[149] (XLIV),[150,151] and also tricarbonyl(acenaphthylene)chromium, acenaphthylenebistricarbonyliron[152], and others.

Scheme 10



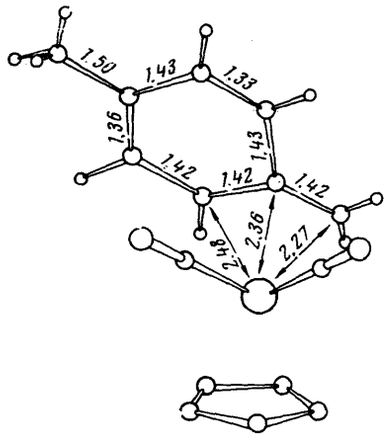
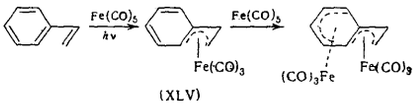


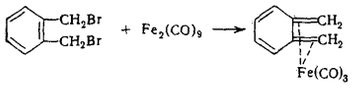
Figure 8. Structure of dicarbonyl(π-*p*-isopropylbenzyl)-cyclopentadienylmolybdenum[141].

After the structure of the π-benzyl derivatives had been established, and confirmed the breakdown in the aromatic character of this ligand, interest in such compounds grew. New examples of fragmentary coordination were found, sometimes involving fundamental reconstruction of the whole system. It was shown in particular that under severe conditions even styrene could be dismembered (formally) into two butadiene units, each of which combined with a tricarbonyliron group[153-155]:



(XLV)

If the aromatic molecule contains substituents capable of interacting with the metal, the rearrangement of the ligand may become more fundamental, as shown above in the reactions of 2-bromomethylnaphthalene and of brominated xylene with iron carbonyl[156]:



Thus an aromatic molecule is undoubtedly able to yield π-complexes involving not only the whole system of delocalised π-electrons but even part of this system.

If the π-systems of the fragments thereby become completely independent, a significant loss of delocalisation energy should occur. Calculation shows e.g. that in the formation of (XXXIX) and (XLV) such loss would exceed 1.4 β, and will be 1.23 β and 1.91 β in the formation of (XLI) and (XLII) respectively. Nevertheless, in individual cases complexes are obtained under comparatively mild conditions. This may mean that the state of the aromatic molecule does not change so strongly, or else that it changes considerably but this loss is balanced by the formation of new bonds.

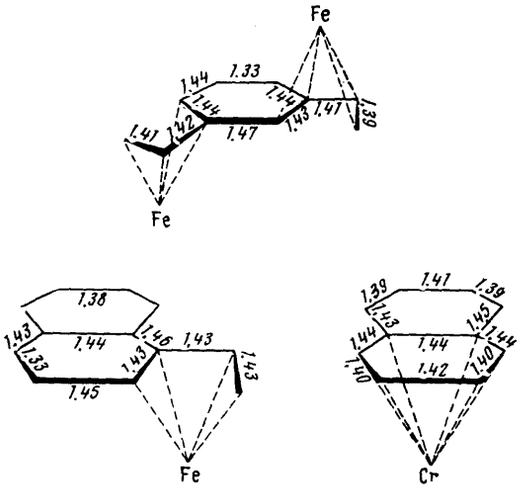


Figure 9. Some structural parameters of complexes of *m*-divinylbenzene with $Fe_2(CO)_6$, vinylnaphthalene with $Fe(CO)_3$, and naphthalene with $Cr(CO)_3$.[158]

Spectral and X-ray investigations of complexes of the benzyl type[141,157] and also of several derivatives mentioned above[158] show that fragmentary coordination may cause some localisation of π-electrons in the remaining free portion of the ring. The parameters involved are given in Figs. 8 and 9. The shortest bonds are 1.33 — 1.36 Å: i.e. they are typically ethylenic.

Comparison of data for tricarbonyl-iron and -chromium derivatives (Fig. 9) shows that the former grouping produces the more significant localisation of bonds. The short-range and long-range spin — spin interaction constants (proton n.m.r.) for these complexes[159,160] also indicate different degrees of localisation of the π-electron system under the influence of tricarbonyliron and tricarbonylchromium groups.

The carbon — carbon distances in the coordinated fragments are typical of each class of derivative. The metal atom in a π-benzyl complex is located somewhat unsymmetrically with respect to the allyl group and closer to the exocyclic atom.

It cannot at present be stated definitely whether the alternation of bonds found for these systems affects their chemical behaviour. An attempt to subject the butadiene portion of the π-benzyl ligand to the Diels — Alder reaction[142] did not give a clear result. This question merits further study; it is extremely important in connection both with the chemistry of aromatic compounds and with the role of the metal.

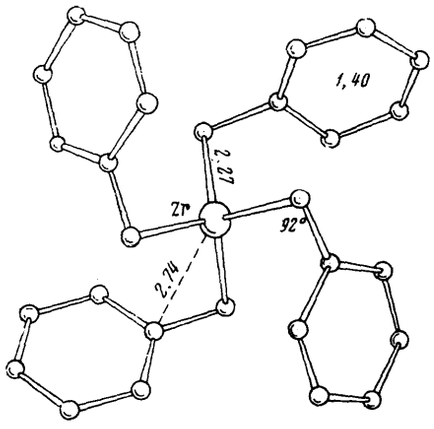


Figure 10. Structure of tetrabenzylzirconium[166].

The n.m.r. spectra of π-benzyl complexes of molybdenum and tungsten depend on the temperature, which indicates that the molecules are flexible[140,142]. At low temperatures (below −30°C) the spectrum is consistent with the suggested structure. With rise in temperature, however, it simplifies as a result of the averaging out of three pairs of protons—the two methylene protons and the ring *oo'*- and *mm'*-protons—by an intramolecular dynamic process assumed[142] to involve production of a σ-form. Quite rapid rotations about CH_2 — Mo and CH_2 — C bonds are possible in such an intermediate compound, which may be responsible for the observed averaging. The process is independent of the nature of the solvent: i.e. decrease in coordination number on passing to the σ-form is not balanced by interaction with the solvent. However, this transition restores the resonance stabilisation, so that energetically a σ-state is entirely probable. Thus the tendency to pass into a dynamic state, which is well known with allylic derivatives of metals, is characteristic also of the π-benzyl type of complexes.

π-Thienyl complexes do not exhibit the properties of flexible systems, but the existence of rotational isomers is not excluded[143].

After the discovery of π-benzyl complexes further investigation became necessary of the nature of the bond in several other benzyl derivatives of metals. The reason for this was their considerably greater stability compared with alkyl and aryl derivatives. For example, the tetrabenzyl derivatives of vanadium[161], titanium[162-164], and zirconium[165,166] have been prepared. The latter two compounds are stable, and have been studied by X-ray diffraction. Although a π-benzyl form was not confirmed in this case, the structure has noteworthy features (Fig. 10). In both cases the molecule is a distorted tetrahedron. All seven atoms within the benzyl groups are coplanar, their plane being almost perpendicular to the M — CH_2 bonds. All the M — CH_2 — C angles are significantly smaller than tetrahedral, while the distance (2.74 Å) from the metal to the first carbon atom of the ring is shorter than would be expected for a true σ-structure. The electron system of this atom is probably able to interact with vacant orbitals of the metal. According to the n.m.r. results this interaction is maintained even in solution[164].

Great interest attaches also to the extraordinarily stable triphenylmethyl derivatives of nickel—$[(C_6H_5)_3C]_2Ni$ [167] and $(C_6H_5)_3CNiCl$ [168]—on which no structural investigations have been made.

In concluding this Section mention must be made of the surprising lithium complex $C_6H_5CH_2Li.2N(CH_2CH_2)_3N$† containing a benzyl ligand and two amine molecules. Its structure[169] is analogous to the π-complex of molybdenum: i.e. it contains a π-bonded ligand. π-Complexes are not characteristic of non-transition metals; π-complexes involving separate fragments of an aromatic system are still less characteristic .

The main aim of this Review is to direct the attention of chemists of various kinds, including theoreticians, to the new opportunities and new problems which are opening up in the organic chemistry of the transition metals. The problems raised cannot be solved without combining many endeavours. The Reviewer will have achieved her aim if interest in these problems is aroused and maintained.

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[† 1,4-Diazabicyclo[2,2,2]octane (triethylenediamine) (Ed. of Translation).]

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